$$C_6H_5C\overset{+}{=}NC_6H_5 \ BF_4^- \quad (5)$$

Experimental Section

Nuclear magnetic resonance spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer, using CD_2Cl_2 as a solvent and lock in 5-mm tubes. ^1H chemical shifts are related to the center of the triplet of $CHDCl_2$, taken to be 5.32 ppm from external Me_4Si. ^{13}C chemical shifts are related to the center of the quintet of CD_2Cl_2, taken to be 53.8 ppm from external Me_4Si. Infrared spectra were obtained on a Pye Unicam SP3-200 instrument with 0.1-mm NaCl cells.

Complex 1 was prepared by passing gaseous boron trifluoride into a solution of 0.25 mmol of benzonitrile in 0.4 mL of CD_2Cl_2 at 0 °C until the formation of the benzonitrile–BF_3 adduct[9] was complete. The protons of the adduct resonate at ca. 0.3 ppm farther downfield than do those of the free nitrile, and the $C\equiv N$ vibration which occurs at 2215 cm^{-1} in the free nitrile appears at 2300 cm^{-1} in the adduct. Addition of 0.25 mmol of neat 2-propanol to the solution produced the complex 1: ^1H NMR δ 8.01 (1 H, br s), 7.8–7.2 (5 H, m), 4.71 (1 H, septet, J = 6.4 Hz), 1.48 (6 H, d, J = 6.4 Hz); ^{13}C NMR δ 134.2, 132.9, 129.7, 119.0, 111.4, 75.5, 22.4; IR (CH_2Cl_2) 3565, 3400, 3060, 2975, 2740, 2245, 1490, 1390, 1380, 1155, 867 cm^{-1}. The ^1H and ^{13}C NMR spectra were essentially identical at 0 and 37 °C. The same spectra were obtained when boron trifluoride was passed into a solution containing equimolar quantities of nitrile and alcohol. Addition of water to these solutions yielded only recovered nitrile and alcohol.

Rearrangement of 1 to 3. After a solution of 1 in CD_2Cl_2 was allowed to stand at room temperature for 65 days, the ^1H NMR spectrum had completely changed to that of complex 3, identical with that formed from a known sample of *N*-isopropylbenzamide: δ 7.8–7.4 (5 H, m), 4.45 and 4.36 (1 H total, pair of overlapping septets of almost equal intensity, both with J = 6.6 Hz), 1.34 (6 H, d, J = 6.6 Hz). Solutions of this complex were stable for several weeks at room temperature.

N-Isopropylbenzonitrilium tetrafluoroborate (2) was prepared by stirring 0.50 mmol of benzonitrile and 0.50 mmol of 2-bromopropane with 0.55 mmol of silver tetrafluoroborate (PCR) in 0.7 mL of CD_2Cl_2 for 3.5 h at room temperature; ^1H NMR δ 8.3–7.2 (5 H, m), 4.90 (1 H, septet, J = 6.6 Hz), 1.70 (6 H, d, J = 6.6 Hz). Addition of water to the solution of 2 gave a single product whose ^1H NMR and IR spectra were identical with those of a known sample of *N*-isopropylbenzamide.

Synthesis of 2,2,2-Trifluoroethanesulfonic Acid

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Introduction

A literature search indicated several probable methods for the preparation of fluoroalkanesulfonic acids. In one of these methods, Haszeldine and Kidd[1] oxidized (CF_3-

(1) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* 1954, 4228.

**Scheme I. Preparation of
2,2,2-Trifluoroethanesulfonic Acid**
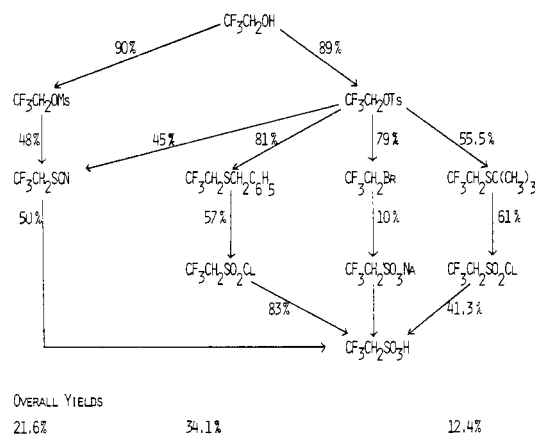
$S)_2Hg$ with 35% hydrogen peroxide at 105 °C.

The end product of the oxidation of mercaptans, sulfides, disulfides, sulfones, etc. is a sulfonic acid. Oxidation by potassium permanganate,[2] chromic anhydride,[2] bromine–water,[3,4] hydrogen peroxide,[5] nitric acid,[6] and alkalis[7] is reported.

Many halogen compounds react with sodium, potassium, or ammonium sulfites to give high yields of sulfonic acid salts,[8–10] i.e., alkylation of alkali sulfites (Strecker).

Results and Discussion

The first method selected for evaluation was Strecker's method. It is commonly used for the synthesis of nonfluorinated alkanesulfonic acids. By use of this procedure, the reaction of CF_3CH_2Br and Na_2SO_3, conducted in a Parr pressure reactor because of its very low boiling point (25 °C), produced a complicated mixture. The yields varied from 5 to 10% and purification of the sulfonate salt was very difficult.

The second method involved the oxidation of CF_3CH_2SCN. The latter was obtained from CF_3CH_2OH by converting it into mesylate according to Crossland and Servis[11] or to the tosylate, a method described by Edgell and Parts.[12] These products were then reacted with NaSCN according to Crossland, Wells, and Shiner[13] to yield the corresponding thiocyanate. We found that the nitric acid oxidation of the crude thiocyanate compound gave $CF_3CH_2SO_3H$ of high purity, but the overall yield was only 20%.

2,2,2-Trifluoroethanesulfonic acid was also prepared by the introduction of sulfur into CF_3CH_2OH with subsequent oxidation to the respective sulfonic acid. This was accomplished by reacting the CF_3CH_2OTs with the sodium salt of benzyl or *tert*-butyl mercaptan to yield the corresponding $CF_3CH_2SCH_2C_6H_5$ or $CF_3CH_2SC(CH_3)_3$. These sulfides were then subjected to oxidative chlorination to

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(5) Boaker, *Recl. Trav. Chim. Pays-Bas* **1935**, *54*, 205.
(6) Murray *J. Chem. Soc.* **1933**, 739.
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(11) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.
(12) Edgell, W. F.; Parts, L. *J. Am. Chem. Soc.* **1955**, *77*, 4899.
(13) Crossland, R. K.; Wells, W. E.; Shiner, V. J. *J. Am. Chem. Soc.* **1971**, *93*, 4217.

give the corresponding sulfonyl chlorides which were subsequently hydrolyzed with water to sulfonic acids. Of the two possible routes, the one utilizing the benzyl mercaptan proved to be the most efficient with much higher yields.

The results described above are summarized in Scheme I.

Experimental Section

All melting points are uncorrected. The NMR spectra were recorded on a Varian Associates A-60 spectrometer.

CF_3CH_2OMs was prepared by the method described by Crossland and Servis:[11] 90% yield; bp 97–99 °C (35 mmHg); NMR (CD_3COCD_3) δ 3.24 (s, 3 H), 4.75 (q, 2 H, $J_{H,F}$ = 8.4 Hz).

CF_3CH_2OTs was prepared by the method described by Edgell and Parts:[12] 89% yield; bp 102–104 °C (0.8 mmHg); mp 40–41 °C; NMR (CD_3COCD_3) δ 6.6 (q, 4 H), 3.5 (q, 2 H), 1.5 (s, 3 H).

CF_3CH_2Br was prepared by the method described by Henne and Ruh:[14] 79% yield; bp 25.5–26 °C.

Reaction of CF_3CH_2Br with Na_2SO_3 in a Parr Pressure Reactor. A solution of 40 g (0.32 mol) of Na_2SO_3 dissolved in 200 mL of water and 48.6 g (0.3 mol) of CF_3CH_2Br was placed in a 1-L Parr pressure reactor and slowly heated with stirring. Usually at about 90 °C an exothermic process subsided, and the reactor was heated at 100 °C for 12–16 h. The reaction mixture was cooled, the unreacted bromide (if present) separated, the aqueous solution evaporated to dryness, and the solid residue extracted with hot EtOH. Evaporation of ethanol gave the crude sodium salt of $CF_3CH_2SO_3H$. The approximate yield is based on the amounts of crude sulfonate salt isolated. The IR spectra showed distinct absorptions at 1160 and 1060 cm^{-1} characteristic of sulfonic acid salts.

Preparation of 2,2,2-Trifluoroethyl Thiocyanate. A. From CF_3CH_2OMs. A solution of 145.8 g (1.8 mol) of NaSCN in 350 mL of DMF was brought to reflux and distilled through a 7-in. column packed with helices until the head temperature reached 152 °C. CF_3CH_2OMs (79.5 g, 0.45 mol) was added to the cooled solution. The reaction mixture was very slowly distilled, and the reaction boiling at 90–123 °C was collected over a period of 2.5–3 h. The distillate was taken up in 300 mL of CH_2Cl_2, washed several times with 100-mL aliquots of water and twice with brine, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue vacuum distilled. The fraction boiling at 55–70 °C (30 mmHg) was collected. NMR (CD_3COCD_3) showed about 80% content of the thiocyanate [δ 3.45 (q, 2 H, $J_{H,F}$ = 10 Hz)]. The yield of the product corrected for impurities was 31.1 g (48%).

B. From CF_3CH_2OTs. In a similar manner, 76.2 g (0.3 mol) of CF_3CH_2OTs, 97.2 g (1.2 mol) of NaSCN, and 200 mL of CH_2Cl_2 yielded 19.1 g (45%) of the thiocyanate, bp 57–72 °C (35 mmHg).

Oxidation of CF_3CH_2SCN with Nitric Acid. Concentrated nitric acid (182 mL, 2.77 mol) was placed in a three-necked flask supplied with mechanical stirrer, dropping funnel, thermometer, reflux condenser, and a nitrogen inlet tube. CF_3CH_2SCN was added (30 g, 0.21 mol) very slowly (over 4 h) at 80–90 °C. Nitrogen was continuously bubbled through the reaction mixture to remove the nitrogen oxides formed. The reaction mixture was then heated at 90–95 °C (steam bath) until the evolution of NO_2 ceased (about 12 h). It was then transferred to an evaporating dish and heated on a steam bath. The thick, oily residue was transferred into a distillation flask and vacuum distilled, yielding 17.2 g (50%) of $CF_3CH_2SO_3H$. The product is a colorless, hygroscopic solid: bp 108–110 °C (1.5 mmHg); mp 50–51 °C; neutralization equivalent 162 (calcd 164); NMR (D_2O) δ 3.85 (q, 2 H, $J_{H,F}$ = 10 Hz).

Reaction of CF_3CH_2OTs with Benzyl and tert-Butyl Mercaptan. In a three-necked flask fitted with mechanical stirrer, thermometer, reflux condenser, and dropping funnel were placed 16 g (0.20 mol) of 50% NaOH and 60 mL of DMF. The mixture was flushed well with N_2 and 24.8 g (0.20 mol) of benzyl mercaptan was added. When homogeneous, the warm solution was treated with 43.2 g (0.17 mol) of CF_3CH_2OTs at such a rate as to maintain the reaction temperature at 55–65 °C. The solution turned cloudy,

and the stirring was continued until the temperature dropped to about 30 °C. The reaction mixture was quenched in 250 mL of water, the product was extracted with CH_2Cl_2, and the organic layer was washed with dilute NaOH and water and dried over anhydrous $MgSO_4$. The solvent was evaporated, and residue vacuum distilled to give 28.3 g (81%) of $CF_3CH_2SCH_2C_6H_5$: bp 45–46 °C (20 mmHg); NMR (CCl_4) δ 2.68 (q, 2 H, methylene, $J_{H,F}$ = 10 Hz), 3.61 (s, 2 H, benzyl), 7.14 (s, 5 H, aromatic).

In a similar fashion, 0.34 mol of 50% NaOH, 125 mL of DMF, 30.7 g of tert-butyl mercaptan, and 0.17 mol of CF_3CH_2OTs gave 16.2 g (55%) of tert-butyl 2,2,2-trifluoroethyl sulfide: bp 70–72 °C (100 mmHg); NMR (neat) δ 1.30 (s, 9 H, tert-butyl), 3.10 (q, 2 H, methylene, $J_{H,F}$ = 11 Hz).

Oxidation of Sulfides with Chlorine in Water. In a three-necked flask equipped with mechanical stirrer, thermometer, reflux condenser, and chlorine inlet tube were placed 0.12 mol of the preceding sulfide and 50 mL of water. The mixture was cooled in a dry ice–acetone bath. At 0 °C, with ice beginning to form on the walls, gaseous chlorine was added above the mixture, controlling the temperature from –5 to 0 °C generally, with –10 °C reached toward the end. Chlorine was introduced until saturation was obtained. The lower layer was mixed with 10 mL of CH_2Cl_2, drained, and chilled while being dried over anhydrous $MgSO_4$. Solvent was removed, and the residue distilled under reduced pressure to give $CF_3CH_2SO_2Cl$. (a) From benzyl 2,2,2-trifluoroethyl sulfide: yield 57%, bp 65–67 °C (45 mmHg); the product was contaminated with a small amount of benzyl chloride. (b) From tert-butyl 2,2,2-trifluoroethyl sulfide: yield 61%; bp 57–60 °C (40 mmHg);[11] the product was contaminated by unidentified admixtures which could not be removed by fractional distallation; NMR (neat) δ 4.37 (q, 2 H, $J_{H,F}$ = 9 Hz).

Hydrolysis of $CF_3CH_2SO_2Cl$ to Sulfonic Acid. $CF_3CH_2SO_2Cl$ (0.05 mol), or the appropriate amount of the sulfonyl chloride mixture with $C_6H_5CH_2Cl$, and 20 mL of water were refluxed with stirring for 10 h. After cooling, the solution was extracted twice with 10-mL aliquots of ether, the aqueous layer was evaporated, and then residue was vacuum distilled to give $CF_3CH_2SO_3H$: yield 83%; bp 90–93 °C (0.1 mmHg); neutralization equivalent 167 (calcd 164); NMR (D_2O) δ 3.87 (q, 2 H, $J_{H,F}$ = 10 Hz). Anal. Calcd for $C_8H_{10}O_3NF_3S$ (aniline derivative): C, 37.35; H, 3.89; F, 22.18; S, 12.45. Found: C, 37.13; H, 3.74; F, 22.05; S, 12.16.

Hydrogen Bonding in Carbanions and Nitranions

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Evidence for hydrogen bonding in carbanions is provided by the strong influence that hydroxylic solvent components have on UV[1] and NMR[2] properties of carbanions and on

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